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(54) Polyester compositions containing phthalimidoesters.

(57) Certain phthalimidoesters are useful as plasticizers for polyethylene terephthalate, particularly for polyethylene terephthalate molding compositions containing a reinforcing agent and a nucleating agent.

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Description

POLYESTER COMPOSITIONS CONTAINING PHTHALIMIDOESTERS

Background of the Invention

This invention relates to polyester compositions. Particularly, the invention relates to polyethylene terephthalate compositions containing certain phthalimidoesters, as plasticizers, and more particularly to compositions for molding engineering thermoplastic parts.

Polyalkylene terephthalates have long been used for the manufacture of various molded articles. Such polymers, particularly when combined with reinforcing materials and fillers such as glass fibers, are suitable for the manufacture of engineered thermoplastic molded articles due to their high wear resistance, durability and high dimensional accuracy. These good physical properties are most readily achieved by molding a composition containing reinforcing material, under conditions under which the polyalkylene terephthalates become partially crystalline.

Of the polyalkylene terephthalates, polyethylene terephthalate imparts preferred physical properties in the molded article. However, polyethylene terephthalate is often not the material of choice for injection molding usage because relatively high mold temperatures, e.g., 120°C to 140°C, must be utilized to ensure good moldability and to obtain the desired crystallinity. Because of the high temperatures required, relatively long molding times are necessary. These stringent processing conditions often prevent the use of polyethylene terephthalate for injection molding in spite of its high rigidity and good heat distortion temperature. Other polyester polymers, particularly polybutylene terephthalate require shorter molding times and lower molding temperatures because of their higher inherent rate of crystallization. However, these polymers are inferior to polyethylene terephthalate in their physical properties, particularly in their heat distortion temperature.

Thus, it is desirable to produce a polyethylene terephthalate molding composition that will crystallize at lower temperatures. This lowering of crystallization temperature must be accomplished without unduly adversely affecting the physical properties of the molded articles. Additionally, any additive that improves crystallization must have sufficiently low volatility so that it does not volatilize out of the composition at elevated processing temperatures, and so that it does not cause deposits on the mold surfaces. The phthalimidoesters of the invention reduce the molding time and temperatures of polyethylene terphthalate compositions by improving and reducing the lower temperature at which crystallization occurs during cooling of the melt. Furthermore, such phthalimidoesters also result in polyethylene terephthalate compositions with low volatility, good physical properties, and high gloss.

Summary of the Invention

The present invention provides a polyester composition comprising:

(a) a polyethylene terephthalate having an intrinsic viscosity of at least about 0.4 deciliter/gram measured as a 0.5% by weight solution in a 60:40 mixture of phenol and tetrachloroethane at 25°C; and

(b) a plasticizer comprising phthalimidoester of the formula:

$$X\text{-}A\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}O\text{-}R$$

wherein X is phthalimido, dihydrophthalimido, tetrahydrophthalimido, or hexahydrophthalimido and where A is alkylene, or substituted alkylene with from 1 to 18 carbon atoms and where R is alkyl, alkenyl, substituted alkyl, or substituted alkenyl with from 4 to 20 carbon atoms, or

$$-R'\text{-}O\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}A'\text{-}X'$$

where X' may be the same as or different than X and is phthalimido, dihydrophthalimido, tetrahydrophthalimido or hexahydrophthalimido and where R' is alkylene, alkenylene, substituted alkylene, or substituted alkenylene with from 2 to 20 carbon atoms and A' is alkylene, or substituted alkylene with from 1 to 18 carbon atoms.

If the phthalimidoester is a monophthalimidoester, it is preferred that the number of carbon atoms is A or R total from 5 to 30 carbon atoms. And if the phthalimidoester is a diphthalimidoester, it is preferred that the carbon atoms of A, R' and A' total from 4 to 36 carbon atoms.

It is preferred that the phthalimidoester be at least about 0.1% by weight of the polyethylene terephthalate.

In a preferred embodiment, the present invention comprises a polyester molding composition comprising:

(a) from about 40 to about 95 parts by weight of a polyethylene terephthalate having an intrinsic viscosity of at least about 0.4 deciliter/gram measured as a 0.5% weight solution in a 60:40 mixture of

phenol and tetrachloroethane at 25°C;

(b) from about 0.1 to 15 parts by weight of a plasticizer comprising a phthalimidoester as defined above;

(c) from about 0.1 to about 10.0 parts by weight of a nucleating agent; and

(d) from about 5 to about 60 parts by weight of a reinforcing agent.

This invention also provides a molded, shaped article prepared from the polyester molding composition described above.

This invention also provides a process for the preparation of polyester compositions wherein a polyethylene terephthalate having an intrinsic viscosity of at least about 0.4, preferably at least about 0.6 deciliters per gram is mixed with phthalimidoester as defined above, and homogenized in a melt.

Detailed Description of the Invention

The polyethylene terephthalate used in preparing the polyester compositions of the invention has an intrinsic viscosity of at least about 0.4 deciliters per gram when measured as a 0.5% by weight solution in a 60:40 mixture of phenol and tetrachloroethane at 25°C. It is preferred that the intrinsic viscosity should be about 0.6 deciliters per gram and in some instances an intrinsic viscosity of about 1.0 or more deciliters per gram may be desirable. As used herein, the term "polyethylene terephthalate" includes polyethylene terephthalate as well as polyethylene terephthalate copolymers and polymer blends containing polyethylene terephthalate, provided the copolymer or polymer blend is at least about 60% by weight of polyethylene terephthalate. Preferred copolymers include those in which a portion of the ethylene glycol is replaced by other polyhydric alcohols, including, but not limited to, propylene glycol and butylene glycol, and in which a portion of the terephthalic acid is replaced by other polyfunctional carboxylic acids. Suitable polymer blends include physical mixtures of polyethylene terephthalate with other polymers, particularly other polyesters. The polyethylene terephthalate is used in the molding composition in an amount of from about 50 to about 95 parts by weight, preferably about 60 to about 9 parts by weight.

The phthalimidoester of this invention comprise compounds of the general formula :

$$X-A-\overset{\displaystyle O}{\overset{\|}{C}}-O-R$$

where X is phthalimido, dihydrophthalimido, tetrahydrophthalimido , or hexahydrophthalimido, where A is alkylene or substituted alkylene, with from 1 to 18 carbon atoms, preferably from 1 to 12 carbon atoms, and more preferably, from 1 to 6 carbon atoms, and where R is alkyl, substituted alkyl, alkenyl, or substituted alkenyl with from 4 to 20 carbon atoms preferably from 7 to 18 carbon atoms or

$$R'-O-\overset{\displaystyle O}{\overset{\|}{C}}-A'-X'$$

where X' may be the same as or different than X and is phthalimido, dihydrophthalimido, tetrahydrophthalimido or hexahydrophthalimido and where R' is alkylene alkenylene, substituted alkylene, or substituted alkenylene with from 2 to 20 carbon atoms, preferably from 2 to 10 carbon atoms and A' is alkylene or substituted alkylene with from 1 to 18 carbon atoms, preferably from 1 to 12 carbon atoms, and more preferably, from 1 to 6 carbon atoms.

If the phthalimidoester is a monophthalimidoester, it is preferred that the carbon atoms of A and R total from 5 to 30 carbon atoms, more preferably from 8 to 28 carbon atoms. If the phthalimidoester is a diphthalimidoester, it is preferred that the carbon atoms of A, R', and A' total from 4 to 36 carbon atoms, more preferably from 6 to 28 carbon atoms.

In general, the phthalimidoester is present at least about 0.1% by weight of the polyethylene terephthalate. In a complete molding composition the amount of phthalimidoester ranges from about 0.1 to about 15 parts by weight, preferably, from about 3 to about 10 parts by weight. These phthalimidoester compounds have excellent compatibility with polyethylene terephthalate. However, the concentration of phthalimidoester should be kept below a level at which incompatability may occur under the conditions to which the composition will be exposed.

The phthalimidoesters of this invention can be prepared by any method known in the art. For example, U. S. Patent No. 3,579,363 describes preparation of 2-ethylhexyl phthalimidoacetate by reacting potassium phthalimide and 2-ethylhexyl α-chloroactate. It is preferred that the phthalimidoesters be prepared by reacting phthalic anhydride, dihydrophthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, or mixtures thereof with either an amino acid or a lactam to form the precursor phthalimidocarboxylic acid which is further reacted with an alcohol to form the phthalimidoester. For sake of simplicity, preparation of the phthalimidoester will be discussed in terms of phthalic anhydride starting material, but the discussion also applies to the hydrogenated phthalic anhydrides.

When an amino acid is used, the phthalimidoester may be prepared in a two-step reaction. In the first step, the amino acid is reacted with phthalic anhydride, usually in the presence of a solvent, such as toluene, xylene, or diethylbenzene. to produce the precursor phthalimidocarboxylic acid. In the second step, this intermediate is esterified by reaction with an appropriate alcohol. preferably in the presence of an esterification catalyst, such as stannous oxalate or other esterification catalyst, and preferably in the presence of an entrainer, which removes water released by the esterification reaction, either by reacting with the water or by forming an azeotrope to remove the water from the reaction mixture. A suitable entrainer is diethyl benzene.

The phthalimidoester may also be prepared in a single step by mixing phthalic anhydride, the amino acid, the alcohol, a catalyst, if desired, and a solvent, if desired, and maintaining the reaction mixture at reflux to remove the water as it evolves. Excess alcohol can be used as the solvent and as an entrainer. After the reaction is complete, unreacted alcohol can be removed by steam stripping, which also insolubilizes the stannous oxalate catalyst for easy removal.

Similarly, either a one-step or two-step process can be used with lactams. The one step process is preferred with either amino acids or lactams, because of simplicity, and the ability to avoid introducing a solvent to the reaction mixture. Additionally, if a lactam is used, the reaction proceeds at a higher rate if a one-step process is used.

Any amino acid can be used as a starting material, provided it does not contain substituents that interfere with formation of the phthalimidoester, that render the resulting phthalimidoester incompatible with the polyethylene terephthalate, or that render it ineffective. Examples of suitable amino acids include glycine, α-alanine, β-alanine, aminodecanoic acid, methionine, 3-aminobutyric acid, 6-aminocaproic acid, isoleucine, 2-amino-4-methylpentanoic acid, 2-amino-3-phenylpropionic acid, 2-amino-3-methylbutyric acid, aminooctadecanoic acid, or any other amino acid with a suitable alkylene or substituted alkylene group. A mixture of suitable amino acids can also be used.

Any lactam can be used as a starting material, provided it does not contain susbtituents that interfere with formation of the phthalimidoester or that render the resulting phthalimidoester incompatible with the polyethylene terephthalate or that render it ineffective. Examples of suitable lactams include 2-pyrrolidone, δ-valerolactam, ε-caprolactam, or any other lactam with asuitable alkylene or substituted alkylene group. Mixtures of suitable lactams or of lactams and amino acids can also be used.

When referring to amino acids, lactams, and groups A and A', the phrase alkylene or substituted alkylene is meant to include both straight and branched chain groups as well as groups that contain substituents that do not interfere with formation of the phthalimidoester, and that do not render the resulting phthalimidoester incompatible with the polyetheylene terephthalate or ineffective. Examples of noninterfering substituents include ether and thioether groups.

If monohydric alcohols are used for esterification, monophthalimide compounds result. If dihydric alcohols are used, diphthalimide compounds result. Any monohydric alcohol can be used, provided it has from 4 to 20 carbon atoms, preferably 7 to 18 carbon atoms, and does not contain substituents that interfere with formation of the phthalimidoester or that render the resulting phthalimidoester incompatible with the polyethylene terephthalate or ineffective. Examples of suitable monohydric alcohols include heptanol, octanol, nonanol, decanol, undecanol, dodecanol, octadecanol, or any other suitable monohydric alcohol or mixture of monohydric alcohols. Any dihydric alcohol can be used provided it has from 2 to 20 carbon atoms, preferably from 2 to 10 carbon atoms, and does not contain susbtituents that interfere with formation of the phthalimidoester or that render the resulting phthalimidoester incompatible with the polyethylene terephthalate or ineffective. Examples of suitable dihydric alcohols include ethylene glycol, propylene glycol, neopentyl glycol, 1,4-butylene glycol, 1,6-hexanediol, 1,12-dodecanediol, 2-butene-1,4-diol, diethylene glycol, triethylene glycol, or other suitable glycols or glycol oligomers or mixtures of dihydric alcohols. When referring to the alcohols, or to groups R and R', the phrases alkyl, alkenyl, alkylene, substituted alkylene, alkenylene, and substituted alkenylene are meant to include both straight and branched chain groups, as well as groups that contain other substituents that do not interfere with formation of the phthalimidoester, or render the resulting phthalimidoester either incompatible with the polyethylene terephthalate or inactive.

Mixtures of monohydric or dihydric alcohols can also be used, which will result in a product that is a mixture of monophthalimidoester and diphthalimidoester.

Any nucleating agents suitable for use in polyalkylene terephthalate molding compositions may be utilized in the molding compositions of the invention. All that is required is that the nucleating agent promotes nucleation of the polyalkylene terephthalate crystals. Most nucleating agents raise the upper temperature at which crystallization of the polyethylene terephthalate occurs as the melt cools. Suitable nucleating agents include organic and inorganic nucleators.

Inorganic nucleating agents include calcium salts, such as calcium terephthalate, calcium titanate, calcium pyrophosphate, calcium silicate, calcium benzoate, calcium oxide, calcium carbonate, calcium fluoride, calcium aluminosilicate, and the like. Sodium salts, such as sodium silicate, sodium phenyl phosphate, and sodium aluminosilicate may be used. Other inorganic nucleating agents include salts of other metals, such as lithium, potassium, rubidium and cesium, as well as other inorganic compounds such as zinc borate and zeolites.

One suitable class of inorganic nucleating agents include monovalent metal salts of oxides of carbon, silicon, germanium, tin, and lead. The preferred oxides are those of carbon and silicon, with carbon oxides such as carbonate and bicarbonate being particularly preferred. Preferred monovalent metals include lithium,

sodium, potassium, rubidium, and cesium, with lithium, sodium and potassium being preferred, and sodium being particularly preferred.

Other suitable nucleating agents include the sodium or potassium, or other metal salts of hydrocarbon carboxylic acids. One class of suitable carboxylic acids contains between 7 and 25 carbon atoms, preferably more than 12 carbon atoms. Representative of these carboxylic acids are fatty acids, such as stearic, pelargonic and behenic acid. Additionally, salts of ethylenediaminetetraacetic acid may be suitable nucleating agents, particularly the sodium salt. These carboxylic acid salts also include the sodium or potassium salts of carboxyl containing organic polymers, either fully or partially neutralized, such as copolymers of olefins or aromatic olefins with acrylic or methacrylic acids or maleic anhydride. These polymeric materials include, for example, the sodium or potassium salt of ethylene methacrylic acid copolymers or styrene maleic anhydride copolymers, including both wholly or partially neutralized salts of each. In the copolymers above, the olefin or aromatic olefin moiety ordinarily comprises 50% to 98% by weight of the copolymer and, preferably, 80% to 98%. An especially preferred polymeric material is the sodium salt of ethylene methacrylic acid copolymer. Also included are salts of oligomers of unsaturated fatty acids, particularly dimers and trimers of C_{18} fatty acids, commonly known as "dimer acid" and "trimer acid."

A preferred class of nucleators, whether organic or inorganic, is alkali metal salts and mixed salts containing alkali metals. Preferred alkali metals are sodium and potassium, with sodium being particularly preferred.

In general, any suitable reinforcing agent can be used in the molding compositions of the invention. The reinforcing agent may optionally be treated with various coupling agents or adhesion promoters in a manner in which is well known to those skilled in the art. Examples of suitable reinforcing agents include glass fibers, carbon fibers and filaments, aramid fibers, alumina, feldspar, asbestos, talc, calcium carbonates, clay carbon black, quartz, novaculite and other forms of silica, galenite, bentonite, garnet, mica, saponite, beidellite, titanium dioxide and titanate whiskers, aluminum, iron or nickel fibers, whiskers or platelets, vermiculite, calcium metasilicate, and the like. In particular, the preferred reinforcing agent is glass fiber, more particularly glass fibers, comprised of lime-aluminum borosilicate glass that is relatively sodium free, commonly known as "E" glass. In some instances, it also may be desirable to use a mixture of reinforcing agents such as a mixture of glass fibers and mica.

Other optional additives may be included in the compositions of the invention. For example, the compositions of the invention may also include a chain extender which helps to compensate for polyester chains which are broken by hydrolysis with resulting molecular weight degradation. Such chain extenders include, for example, carbodiimides and polyepoxides. Epoxy resins, which are preferred, include an epoxy formed from bisphenol-A and glycidol ether or polyepoxides obtained by reacting ortho cresol novolac and epichlorohydrin. Especially preferred polyepoxides are epoxy cresol novolac resins. If a chain extender is used, it is preferred that about 0.1 to about 5 parts by weight be used. Other optional additives may include impact modifiers, mold release agents, anti-static agents, coloring agents, such as pigments and dyes, thermal oxidative and light stabilizers, flame retardants and other additives known in the art.

The molding compositions of the invention can be prepared and molded using any conventional or well-known method. For example, in one suitable method the polyalkylene terephthalate and glass fiber are placed into an extrusion compounder to produce molding pellets. In another procedure, the polyalkylene terephthalate and glass are mixed by dry blending, then either milled and communited or extruded and chopped. Alternatively, the ingredients can be mixed with the powdered or granular polyalkylene resin and directly molded by injection or transfer molding techniques. Ordinarily, it is desirable to thoroughly free the ingredients from as much water as possible.

It is preferred that compounding be carried out to ensure that the residence time in the molding machine is short; the temperature is carefully controlled; friction heat is utilized; and an intimate blend between the additives and the polyester resin is obtained.

Although it is not essential, best results are obtained if the ingredients are precompounded, pelletized and then molded. Precompounding can be carried out in conventional equipment. For example, after predrying the polyalkylene terephthalate, e.g., at 130°C for three hours, a single screw extruder may be fed with a dry blend of the polyester resin and the glass and whatever other additives may be used. Alternatively, a twin-screw extrusion machine can be fed with polyalkylene terephthalate, glass fiber and other additives at the feed port In either case, a generally suitable extruder temperature will be about 230°C to 300°C.

The molding compositions of this invention can be molded in any equipment conventionally used for molding engineering thermoplastic compositions, using conventional techniques.

The phthalimidoester compounds of this invention act to improve the crystallization of the polyethylene terephthalates to which they are added by decreasing the temperature to which crystallization will continue upon cooling of the hot melt. Although not intending to be bound by theory, it is believed that the phthalimidoesters improve crystallization by increasing the molecular mobility of the polymer chain

Additionally, the phthalimidoesters of this invention result in improved melt flow and in improved processability of polyethylene terephthalate compositions, intended for molding or other applications. As a result, the phthalimidoesters can also be considered to be a flow aid or processing aid for polyethylene terephthalate.

Because the phthalimidoesters of this invention decrease the temperature at which crystallization occurs, good heat distortion temperatures (HDT), gloss and other physical properties can be obtained at a lower molding temperature. Also, smaller amounts of nucleating agents may be used without any loss of nucleating

effectiveness.

The compositions of this invention can be prepared using compounding techniques kncwn in the art. They may either be precompounded and pelletized, or mixed and compounded as part of the molding process. It is preferred to precompound and pelletize the composition prior to molding. Precompounding can be accomplished with a single screw extruder, dual screw extruder, a roller mill, or any other method known to one skilled in the art.

The following examples are illustrative of this invention and are not intended to limit its scope.

In the molding formulations of examples, the following components were used: the polyethylene terephthalate (PET) used had an intrinsic viscosity of about 0.66 deciliters/gram; the indicated plasticizer; as a nucleator, an ethylene/methacrylic acid (85/15 by weight) partially neutralized to a sodium salt, sold by duPont under the tradename Surlyn 8660; as a chain extender, a polyglycidyl ether of orthocresolformaldehyde novolac, sold by Ciba-Geigy Corporation, under the tradename Araldite ECN 1273; and 1/8-inch (0.3175 cm) chopped glass strand, sold by Pittsburgh Plate Glass and designated as product type 3540. Compositions were made using plasticizer at a concentration of 5% by weight based on PET. This formulation, expressed as a percentage of the full formulation is as follows:

	% Plasticizer Based on PET
	5%
PET	65.6
Plasticizer	3.4
Nucleator	0.67
Chain Extender	0.33
Glass	30.0

The dried components were mixed and extruded in a single screw extruder, with a die temperature of about 260°C. The extruded ribbon was cooled, chopped into pellets and dried overnight. The dried. pelletized composition was injection molded into a family mold, at a die temperature of about 275°C and a mold surface temperature of 110°C. The closed time was 30 seconds.

The molded parts were tested to determine heat deflection temperature (HDT) by holding the specimen at two support points separated by five inches (12.7 cm), raising the temperature 2°C per minute, and applying a load of 264 psi (1.26 kPa) at the midpoint. The temperature at which deformation of the specimen reaches 0.01 inches (.0254 cm) is the HDT. This is in accordance with ASTM D648-82. Tensile strength and % elongation were determined using ASTM D638-82. Izod impact was determined using ASTM D256-81, except that untouched test specimens were used. Volatility of the compound PET was determined by heating for 4 hours at 175°C on a rotating rack in a forced draft oven.

The T_{pk} of the composition was determined by placing a sample of a molded part into the sample container of a differential scanning calorimeter, that had been heated to about 290°C. After 2 minutes, the sample container was removed and covered with powdered dry ice to "quench" the sample. The quenched sample was dessicated a minimum of 5 minutes, then returned to the calorimeter that had been cooled to room temperature. The calorimeter was programmed for a 10°C per minute temperature increase under a nitrogen atmosphere. An exotherm was observed between about 100°C and about 125°C. The T_{pk} is the temperature at which heat evolves most rapidly during this exotherm. The T_{pk} gives an indication of the effectiveness of the plasticizer at enhancing crystallization with a lower T_{pk} indicating greater effectiveness.

Additionally, the per se volatility of the indicated plasticizer was determined by thermogravimetric analysis of the neat plasticizer, under air atmosphere, using a thermobalance with a programmed temperature rise of 10°C per minute. The thermobalance produced a plot of weight loss versus temperature. From this plot, the temperature at which volatility losses began was determined, as well as the weight percent loss at 300°C and 350°C.

EXAMPLE 1

This example illustrates the stepwise preparation of undecyl 3-phthalimidoproprionate by the initial preparation and isolation of the precursor acid 3-phthalimidopropionic acid, followed by esterification with undecyl alcohol.

A 500 ml flask, equipped with a stirrer, thermometer, and water-separating condenser, was charged with 0.5 mole of β-alanine and 170 ml of xylene. This mixture was stirred and the temperature maintained at 110°-120°C as 0.5 moles of phthalic anhydride was added in portions over 50 minutes. Warming was continued at reflux until water was no longer collected. The reaction mixture was then cooled to room temperature, filtered and the solid washed with xylene and dried. The product was 3-phthalimidopropionic acid, with a melting point of 138°-146°C.

A 0.44 mole portion of the precursor acid, 0.5 moles of undecyl alcohol, 0.3g of stannous oxalate catalyst, and 50 g of diethylbenzene entrainer were charged to the equipment described above. This mixture was

warmed at 210°C. with pressure reduced to maintain reflux, until water was no longer collected. The reaction mixture was then steam-stripped at 165°C and 30 mm Hg, and the product was filtered, giving a 94.5% overall yield of undecyl 3-phthalimidopropionate.

EXAMPLE 2

This example describes the one step production of undecyl 3-phthalimidopropionate in which all the reactants were charged initially.

A 1-liter flask, equipped as in Example 1 was charged with 1.0 mole of phthalic anhydride, 1.0 moles of β-alanine, 1.15 moles of undecyl alcohol, and 0.7g of stannous oxalate. The mixture was warmed to 210° C and kept at this temperature, with the pressure reduced to maintain reflux, until water was no longer collected. The reaction mixture was then steam-stripped as in Example 1, and the product was filtered, giving a 99.6% yield of undecyl 3-phthalimidopropionate.

EXAMPLE 3

This example describes the stepwise preparation of undecyl 6-phthalimidohexanoate by the initial preparation and isolation of the precursor acid, 6-phthalimidohexanoic acid, followed by esterification with undecyl alcohol.

A 1-liter flask equipped as in Example 1 was charged with 0.76 moles of 6-aminohexanoic acid and 250 ml of xylene. This mixture was stirred and the temperature was maintained at 115°C-120°C as 0.76 moles of phthalic anhydride was added in portions over 25 minutes. The reaction mixture was warmed at reflux until water was no longer collected. More xylene was added to aid stirring when the mixture cooled to room temperature. The reaction mixture was filtered, and the solid was washed with xylene and dried to give an 84.5% yield of 6-phthalimidohexanoic acid with a melting point of 105°-110°C.

A 0.59 mole portion of the precursor acid, 0.6 moles of undecyl alcohol, 0.5g of stannous oxalate catalyst, and 50 g of diethylbenzene entrainer were charged to the equipment described above. This mixture was warmed at 210°C, with the pressure reduced to maintain reflux, until water was no longer collected. The reaction mixture was then steam-stripped as in Example 1 and the product was filtered to isolate the undecyl 6-phthalimidohexanoate.

EXAMPLE 4

This example describes the use of ε-caprolactam and the simultaneous charging of all three reactants to produce undecyl 6-phthalimidohexanoate, without isolation of the intermediate acid.

The equipment used in Example 1 was charged with 0.89 moles of ε-caprolactam, 0.89 moles of phthalic anhydride, 0.92 moles of undecyl alcohol, and 60g of diethylbenzene entrainer. This mixture was warmed at 175°C for 1 hour and then 0.7g of stannous oxalate catalyst was added and warming was continued at 210° C for 3 hours with the pressure reduced to maintain reflux. 10g more of undecyl alcohol was added, and refluxing was continued. The reaction mixture was steam-stripped as above and filtered, resulting in a mixture of approximately 95% undecyl 6-phthalimidohexanoate and 5% other components.

EXAMPLE 5

Octadecyl 3-phthalimidopropionate was prepared by a procedure similar to that used in Example 1, except that the intermediate acid was not isolated before it was esterified with octadecyl alcohol. The product had a proton NMR spectrum that was consistent with the desired structure.

EXAMPLE 6

Octadecyl 6-phthalimidohexanoate was prepared from phthalic anhydride, ε-caprolactam, and octadecyl alcohol by a procedure similar to that used in Example 4. The product has a proton NMR spectrum consistent with the desired structure.

EXAMPLE 7

Octadecyl 11-phthalimidoundecanoate was prepared from phthalic anhydride, 11-aminoundecanoic acid, and undecyl alcohol by a procedure similar to that used in Example 1, except that the intermediate acid was not isolated before it was esterified. The product had a proton NMR spectrum that was consistent with the desired structure.

EXAMPLE 8

Undecyl 2-phthalimido-4-(methylthio)butyrate was prepared from phthalic anhydride, DL-methionine, and undecyl alcohol by a procedure similar to that used in Example 1, except that the intermediate acid was not isolated before it was esterified. The product had a proton NMR spectrum consistent with the desired structure.

EXAMPLE 9

Octadecyl 2-phthalimidoacetate was prepared from phthalic anhydride, glycine and octadecyl alcohol by a procedure similar to that used in Example 1, except that the intermediate acid was not isolated from its reaction medium before it was esterified. The product had a proton NMR spectrum consistent with the desired

structure.

EXAMPLE 10

A mixture of octadecyl and hexadecyl 4-phthalimidobutyrate was prepared from phthalic anhydride 4-aminobutyric acid, and tallow-derived C_{16-18} alcohol by a procedure similar to that used in Example 1 except that the intermediate acid was not isolated from the reaction mixture before it was esterified. The product had a proton NMR spectrum consistent with the desired structure.

EXAMPLE 11

Undecyl 2-phthalimidopropionate was prepared from phthalic anhydride, DL-alanine, and undecyl alcohol by a procedure similar to that used in Example 1, except that the intermediate acid was not isolated from its reaction medium before it was esterfied. The resultant product had a proton NMR spectrum consistent with the desired structure.

EXAMPLE 12

A mixture of heptyl, nonyl, and undecyl 6-phthalimidohexanoates was prepared from phthalic anhydride, ε-caprolactam, and a mixture of about 30% C_7 alcohol, about 40% C_9 alcohol, and about 30% C_{11} alcohol, by a procedure similar to that used in Example 4. The product had a proton NMR spectrum consistent with the desired structure.

EXAMPLE 13

2-Ethylhexyl 6-phthalimidohexanoate was prepared from phthalic anhydride, ε-caprolactam and 2-ethylhexyl alcohol by a procedure similar to that used in Example 4. The product had a proton NMR spectrum consistent with the desired structure.

EXAMPLE 14

Dodecyl 6-phthalimidohexanoate was prepared from phthalic anhydride, ε-caprolactam, and dodecyl alcohol by a procedure similar to that used in Example 4. The product had a proton NMR spectrum consistent with the desired structure.

EXAMPLE 15

Undecyl 2-phthalimidoacetate was prepared by adding 2.2 moles of undecyl alcohol to a suspension of 2 moles of 2-phthalimidoacetic acid in xylene. The mixture was stirred and warmed, allowing xylene and the water of reaction to distill until a pot temperature of 210°C was reached at a pressure of about 250 mm Hg. Refluxing at this temperature was continued until water no longer was produced. The reaction mixture was steam-stripped as above and filtered yielding a product having a proton NMR spectrum consistent with the desired structure.

EXAMPLE 16

The di(3-phthalimidopropionate) diester of 2,2-dimethyl-1,3-propanediol was prepared with phthalic anhydride, β-alanine and the dihydric alcohol by a procedure similar to that used in Example 1. The product had a melting point of 158-162°C, and its proton NMR spectrum was consistent with the desired structure.

EXAMPLE 17

The di(6-phthalimidohexanoate) diester of 2,2-dimethyl-1,3-propanediol was prepared from phthalic anhydride, 6-aminohexanoic acid, and the dihydric alcohol by a procedure similar to that used in Example 1 except that the intermediate acid was not isolated from its reaction medium before it was esterified. The product had a proton NMR spectrum that was consistent with the desired structure.

EXAMPLE 18

The di(6-phthalimidohexanoate) diester of triethyleneglycol was prepared from phthalic anhydride, β-caprolactam, and triethyleneglycol by a procedure similar to that used in Example 4. The product was a clear amber liquid having a proton NMR spectrum that was consistent with the desired structure.

EXAMPLE 19

Undecyl 6-tetrahydrophthalimidohexanoate was prepared from 1.2 moles of 1,2,3,6-tetrahydrophthalic anhydride, 1.2 moles of ε-caprolactam, and 1.56 of undecanol in a 1-liter flask equipped as in Example 1. The mixture was warmed at 180°C under nitrogen for 1$^1/_2$ hours and 0.7g of stannous oxalate catalyst was added. The mixture was heated to 250°C for 3$^1/_2$ hours with the pressure reduced to maintain reflux. About 21 ml of water was collected. The reaction mixture was then steam stripped at 175°C and 10 mm Hg for 2 hours, followed by continued stripping without steam for $^1/_2$ hour. The mixture was filtered giving a clear yellow liquid product. The product had a proton NMR that was consistent with the desired structure.

The products of the synthesis examples above were formulated into polyethylene terephthalate molding compositions and were molded as described above. Various of the phthalimidoesters were tested in groups, some of which were compared with similar compositions made using a mixture of C_{14}, C_{16}, and C_{18} N-alkyl,

toluenesulfonamide (TSA), and some were compared with similar formulations using no plasticizer. The properties of the plasticizers and of the formulated PET are reported in Tables I through V below.

TABLE I

Ex. No.	Mol. Wt.	Melting Point (°C)	Plasticizer Volatility: Loss Begins (°C)	% Loss 300°C	% Loss 350°C	T_{pk}(°C)	HDT(°C)	Izod Impact (ft.lbs/in)	Tensile Properties: Strength (psi)	% Elong.	PET Form. at 175°C (mg/sq.cm)
1	374	50-57	215	18	49	107.5	214	13.4	19,250	2.0	0.82
3	416	RT*	200	56	88	106.5	210	12.3	19,250	2.0	0.72
5	472	73-79	225	13	45	107.0	219	13.5	19,250	2.0	0.41
7	485	43-48	240	10	31	106.0	210	12.5	19,500	2.0	0.34
TSA	418	68-70	265	2	16	107	218	13.3	19,500	2.0	0.52

*Room temperature

TABLE II

Ex. No.	Mol. Wt.	Melting Point (°C)	Plasticizer Volatility: Loss Begins (°C)	% Loss 300°C	% Loss 350°C	T_{pk}(°C)	HDT(°C)	Izod Impact (ft.lbs/in)	Tensile Properties: Strength (psi)	% Elong.	PET Form. at 175°C (mg/sq.cm)
17	591	Liquid*	290	1	6	110.5	207	12.6	19,950	2.0	0.27
6	514	47	190	35	73	107.0	218	12.7	19,100	2.0	0.36
16	507	158-162	310	0	5	112.0	206	12.2	19,600	1.9	0.23
None			-	-	-	120.0	207	12.2	18,350	1.9	0.07
TSA	418	68-70	265	2	16	107.0	211	12.2	19,450	2.0	0.48

*Room temperature

TABLE III

Ex. No.	Mol. Wt.	Melting Point (°C)	Plasticizer Volatility: Loss Begins (°C)	Plasticizer Volatility: % Loss 300°C	Plasticizer Volatility: % Loss 350°C	T_{pk} (°C)	HDT (°C)	Izod Impact (ft.lbs/in)	Tensile Properties: Strength (psi)	Tensile Properties: % Elong.	PET Form. at 175°C (mg/sq.cm)
8	434	Liquid*	225	9	43	108.0	218	10.7	19,500	1.9	0.46
9	458	70-75	235	8	30	108.0	216	11.4	20,350	2.0	0.45
11	374	Liquid*	185	76	96	108.5	221	11.1	20,100	2.0	0.66
12	385	Liquid*	195	74	93	105.0	220	12.1	19,500	2.0	0.80
13	374	Liquid*	190	73	93	106.5	214	12.0	18,400	1.6	0.71
None			-	-	-	119.0	212	14.0	19,000	1.9	0.10
TSA	418	68-70	265	2	16	107.0	216	11.6	20,300	2.0	0.48

*Room temperature

TABLE IV

Ex. No.	Mol. Wt.	Melting Point (°C)	T_{pk}-(°C)	HDT(°C)	Izod Impact (ft.lbs/in)	Tensile Properties Strength (psi)	Tensile Properties % Elong.	PET Form. at 175°C (mg/sq.cm)
14	430	36-38	106.0	214	11.7	19,450	2.0	0.63
15	359	55-64	109.5	214	12.1	19,700	2.0	0.82
18	637	Liquid*	109.5	218	11.3	19,550	1.9	0.22
None	-	-	119.5	202	12.8	18,700	2.0	0.13
TSA	418	68-70	107.5	214	11.7	19,400	2.1	0.54

*Room temperature

TABLE V

Ex. No.	Mol. Wt.	Melting Point (°C)	T_{pk} (°C)	HDT(°C)	Izod Impact (ft.lbs/in)	Tensile Properties Strength (psi)	Tensile Properties % Elong.	PET Form. at 175°C (mg/sq.cm)
19	420	~RT*	107.5	215	12.1	19,100	2.0	0.55
3	416	~RT*	107	214	11.6	19,250	2.2	0.75
TSA	418	68-70	107.5	214	13.1	19,350	2.0	0.50

* Room Temperature

In addition to the compositions discussed above, glass reinforced PET molding compositions were prepared utilizing 2-ethylhexyl 6-tetrahydrophthalimidohexanoate, 2-ethylhexyl 6-hexahydrophthalimidohexa-

noate and TSA. Parts molded from each of these compositions in a mold with a surface temperature of about 107°C exhibited equivalent physical properties, while the two hydrogenated phthalimidoesters produced surface gloss somewhat superior to the TSA control indicting equivalent or greater crystallization than that resulting from the TSA.

The preceding examples are intended to illustrate the current invention and not to limit its scope.

Claims

1. A polyester composition comprising:

(a) a polyethylene terephthalate having an intrinsic viscosity of at least about 0.4 deciliter/gram measured as a 0.5% by weight solution in a 60:40 mixture of phenol and tetrachloroethane at 25°C; and

(b) a plasticizer comprising phthalimidoester of the formula:

$$X-A-\overset{\overset{O}{\|}}{C}-O-R$$

wherein X is phthalimido, dihydrophthalimido, tetrahydrophthalimido, or hexahydrophthalimido and where A is alkylene, or substituted alkylene with from 1 to 18 carbon atoms and where R is alkyl, substituted alkyl, alkenyl, or substituted alkenyl with from 4 to 20 carbon atoms, or

$$R'-O-\overset{\overset{O}{\|}}{C}-A'-X'$$

where X' is the same as or different than X and is phthalimido, dihydrophthalimido, tetrahydrophthalimido or hexahydrophthalimido and where R' is alkylene, alkenylene, substituted alkylene, or substituted alkenylene with from 2 to 20 carbon atoms and A' is alkylene, or substituted alkylene with from 1 to 18 carbon atoms.

2. The composition of Claim 1, wherein the phthalimidoester comprises at least about 0.1% by weight of the polyethylene terephthalate.

3. A polyester molding composition comprising:

(a) from about 40 to about 95 parts by weight of a polyethylene terephthalate having an intrinsic viscosity of at least bout 0.4 deciliter/gram measured as a 0.5% weight solution in a 60:40 mixture of phenol and tetrachloroethane at 25°C;

(b) from about 0.1 to about 15 parts by weight of a plasticizer comprising a phthalimidoester of the formula:

$$X-A-\overset{\overset{O}{\|}}{C}-O-R$$

wherein X is phthalimido, dihydrophthalimido, tetrahydrophthalimido, or hexahydrophthalimido and where A is alkylene, or substituted alkylene with from 1 to 18 carbon atoms and where R is alkyl, substituted alkyl, alkenyl, or substituted alkenyl with from 4 to 20 carbon atoms, or

$$R'-O-\overset{\overset{O}{\|}}{C}-A'-X'$$

where X' is the same as or different than X and is phthalimido, dihydrophthalimido, tetrahydrophthalimido or hexahydrophthalimido and where R' is alkylene, substituted alkylene, alkenylene, or substituted alkenylene with from 2 to 20 carbon atoms and A' is alkylene, or substituted alkylene with from 1 to 18 carbon atoms.

(c) from about 0.1 to about 10.0 parts by weight of a nucleating agent; and

(d) from about 5 to about 60 parts by weight of a reinforcing agent.

4. The composition of Claim 3, wherein A, A' and R' are individually alkylene, and R is alkyl.

5. The composition of Claim 3, wherein the phthalimidoester comprises a monophthalimidoester in

which the total number of carbon atoms of A and R is from 5 to 30 carbon atoms.

6. The composition of Claim 3, wherein the phthalimidoester comprises a diphthalimidoester in which the total number of carbon atoms of A, R' and A' is from 4 to 36 carbon atoms.

7. The composition of Claim 3, wherein the nucleating agent is selected from the salt of a dimer acid, the salt of a trimer acid or the salt of a mixture of a dimer and a trimer acid.

8. The composition of Claim 3, wherein the nucleating agent is a copolymer consisting essentially of 85 wt. % ethylene and 15 wt. % methacrylic acid which has been partially neutralized with sodium ions.

9. The composition of Claim 3, wherein the reinforcing agent is fiberglass.

10. The composition of Claim 3, containing from about 0.1 to about 5 parts by weight of a chain extender.

11. The composition of Claim 10, wherein the chain extender is polyepoxide.

12. The composition of Claim 3, wherein the polyethylene terephthalate has an intrinsic viscosity of at least about 0.6.

13. The composition of Claim 3, wherein the polyethylene terephthalate comprises a mixture of polyetheylene terephthalate and polybutylene terephthalate.

14. The composition of Claim 3, further comprising at least one additive selected from impact modifiers, flow promoters, coloring agents, flame retardants, coupling agents and stabilizers for thermal oxidative and light stabilization in effective amounts.

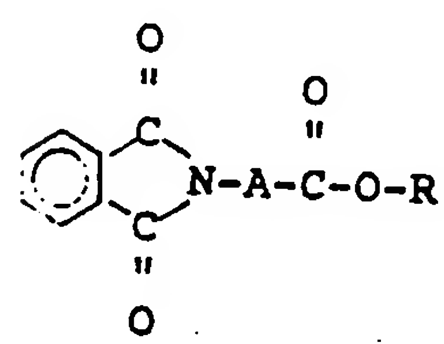
15. A polyester molding composition, comprising:

(a) from about 40 to about 95 parts by weight of polyetheylene terephthalate having an intrinsic viscosity of at least about 0.4 deciliters per gram;

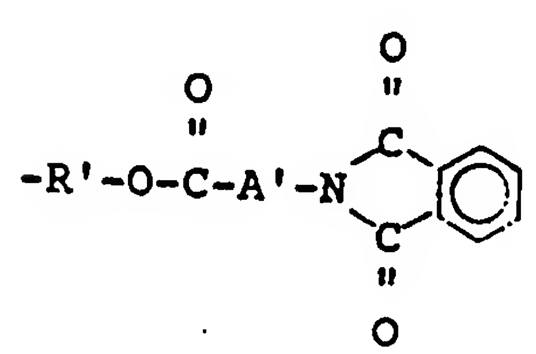
(b) from about 0.5 to about 5.0 parts by weight of a nucleating agent;

(c) from about 5 to about 60 parts by weight of fiberglass;

(d) from about 0.5 to about 15 parts by weight of a plasticizer comprising a phthalimdoester of the formula:



where A is alkylene or with from 1 to 12 carbon atoms and where R is alkyl, or alkenyl with from 4 to 20 carbon atoms, or



where R' is alkylene or alkenylene with from 2 to 10 carbon atoms and A' is alkylene with from 1 to 12 carbon atoms.

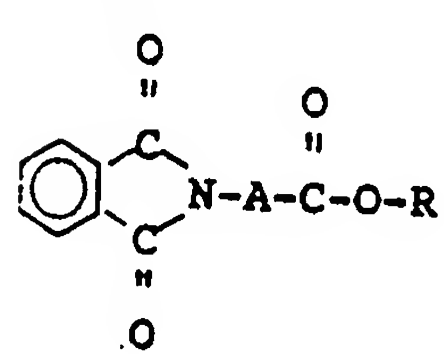
16. A polyester molding composition, comprising:

(a) from about 40 to about 95 parts by weight of polyetheylene terephthalate having an intrinsic viscosity of at least about 0.4 deciliters per gram;

(b) from about 0.5 to about 5.0 parts by weight of a nucleating agent;

(c) from about 5 to about 60 parts by weight of fiberglass;

(d) from about 0.5 to about 15 parts by weight of a plasticizer comprising a phthalimdoester of the formula:



where A is alkylene or substituted alkylene with from 1 to 12 carbon atoms and where R is alkyl, substituted alkyl, alkenyl, or substituted alkenyl with from 4 to 20 carbon atoms.

17. A process for producing a phthalimidoester comprising reacting phthalic anhydride with a lactam in the presence of an alcohol to produce a phthalimidocarboxylic acid, which then reacts with the alcohol to produce the phthalimidoester.